



# Photocatalysis fundamentals revisited to avoid several misconceptions

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## ABSTRACT

Photocatalysis has presently become a major discipline owing to two factors: (i) the intuition of the pioneers of last 20th century and (ii) the mutual enrichment of scientists arising from different fields: photochemistry, electrochemistry, analytical chemistry, radiochemistry, material chemistry, surface science, electronics, and hopefully catalysis. Since heterogeneous photocatalysis belongs to catalysis, all the bases of this discipline must be respected: (i) proportionality of the reaction rate to the mass of catalyst (below the plateau due to a full absorption of photons); (ii) implication of the Langmuir–Hinshelwood mechanism of kinetics with the initial rate being proportional to the coverages  $\theta$  in reactants; (iii) conversions obtained above the *stoichiometric threshold* defined as the maximum number of potential active sites initially present at the surface of a mass  $m$  of titania used in the reaction. In addition, one should respect photonics, with the photocatalytic activity, i.e. the reaction rate being (i) parallel to the absorbance of the photocatalyst and (ii) proportional to the radiant flux  $\Phi$ . In every study, one should determine the quantum yield (QY) (or efficiency), which, although dimensionless, is a “doubly kinetic” magnitude defined as the ratio of the reaction rate  $r$  (in molecules converted/second) to the efficient photonic flux (in photons/second) received by the solid. This is an instantaneous magnitude directly linked to the parameters mentioned above, in particular to the concentration. It can vary from a maximum value of ca. 40% in pure liquid phase to very low values ( $10^{-2}\%$ ) in diluted media (pollutants trace eliminations). To establish true photocatalytic normalized tests, the above recommendations must be observed with a real catalytic activity independent of non-catalytic side-reaction. In particular, dye decolorization, especially in the visible, provides an apparent “disappearance” of the dye, due to a limited stoichiometric electron transfer from the photo-excited dye molecule to titania, subsequently compensated by an additional ionosorption of molecular oxygen. The energetics of photocatalysis on  $\text{TiO}_2$ , being based on the energy  $E$  of the photons, i.e.  $E \geq 3.2$  eV, enables one to produce  $\text{OH}^\bullet$  radicals, the second best oxidizing agent. The decrease of energy  $E$  to the visible may be thermodynamically detrimental for the generation of such highly cracking and degrading species. Concerning solid state chemistry, it is now finally admitted that cationic doping is detrimental for photocatalysis. In conclusion, all these recommendations have to be addressed and experiments have to be operated in suitable conditions before claiming that one deals with a true photocatalytic reaction.

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## 1. Introduction

Heterogeneous photocatalysis has recently appeared as a new emerging “Advanced Oxidation Process” (AOP), with more than 2000 recent publications on the subject at the beginning of the XXIst century [1]. Heterogeneous photocatalysis is simultaneously able to be efficient in Green Chemistry, in Fine Chemicals and in emerging “Advanced Oxidation Processes” (AOP) as recently established [2,3].

When a divided semiconductor is illuminated with photons of energy higher than or equal to its band gap energy, photo-electrons

$e^-$  and photo-holes  $h^+$  are created. In a fluid reaction medium, reactants can adsorb and react either with electrons (acceptor molecules such as  $\text{O}_2$ ) or with holes (donor molecules). Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb reactants and to absorb efficient photons. The 5 main parameters which govern the kinetics are (i) the mass of catalyst, (ii) the wavelength, (iii) the initial concentration (or pressure) of the reactant, (iv) the radiant flux and (v) exceptionally the temperature in extreme conditions with respect to room temperature ( $T < -10^\circ\text{C}$  and  $T > 80\text{--}100^\circ\text{C}$ ).

Initially, photocatalysis originated from different catalysis laboratories in Europe but later received valuable contributions from other chemical sub-disciplines. Photocatalysis has presently become a major discipline owing to two factors: (i) the intuition of the pioneers of last 20th century and (ii) the mutual

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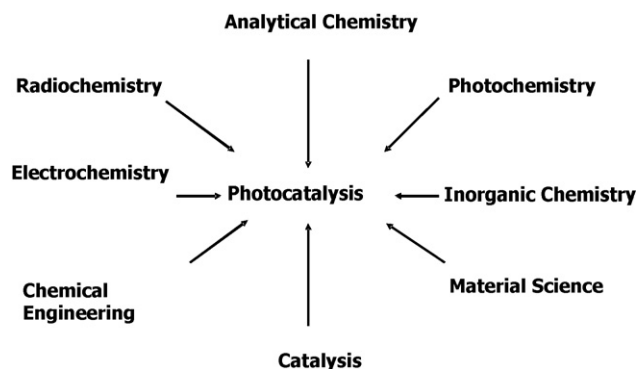


Fig. 1. Contributions to photocatalysis from various sub-disciplines of Chemistry.

enrichment of scientists arising from different fields: photochemistry, electrochemistry, analytical chemistry, radiochemistry, material chemistry, surface science, electronics, and hopefully “catalysis” as illustrated by Fig. 1.

Actually, whereas photocatalysis was developing confidentially in Europe, there was an “earthquake” in Japan, according to Bickley [4] with the re-publication in English of a previous work by Fujishima and Honda on the photo-electrolysis of water using a UV-irradiated titania-based anode [5] in the review “Nature” (238 (1972) 37). Unfortunately, recent scientists in the field of photocatalysis have never read this article and improperly cite it as the starting point of photocatalysis, which is obviously erroneous. Actually, the first reference including the term “photocatalysis” in its title has been published in 1964 by Hauffe in the Journal of Catalysis [6].

## 2. Respect of the fundamentals of heterogeneous catalysis

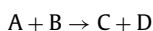
### 2.1. Chemical engineering

Because of the diversity in origins of laboratories working on photocatalysis, there are some misfits and some misconceptions, especially in recent articles originating from laboratories having no culture in heterogeneous catalysis. As in heterogeneous catalysis, heterogeneous photocatalysis follows the 5-step process of chemical engineering, presented in Fig. 2. The only difference with photocatalysis resides in step 3. Instead of thermal activation, photocatalysis implies the activation of the solid by photons. As a consequence, step 3 subsequently includes (i) the absorption of photons by the solid, (ii) the creation of electrons and holes and (iii) the subsequent electron transfer reactions. It has to be noted that the photons must be absorbed by the solid, i.e. their energy  $h\nu$  should be  $\geq E_G$  ( $E_G$  = band gap energy). As a consequence, photocatalysis is quite different from a hypothetical photochemistry in the adsorbed phase.

### 2.2. Langmuir–Hinshelwood mechanism

Often photocatalysis, as heterogeneous catalysis, obeys the Langmuir–Hinshelwood rate form [7] with the rate of reaction  $r$ , chosen as the expression of activity, being proportional to the surface coverages of reactants [2,3,7–10].

In heterogeneous catalysis, for a bimolecular reaction:



rate  $r$  varies as:

$$r = k \theta_A \theta_B$$

Each coverage  $\theta_i$  varies as:

$$\theta_i = \frac{K_i X_i}{1 + K_i X_i}$$

where  $K_i$  is the adsorption constant (in the dark) and  $X_i$  represents either the concentration in the liquid phase or the partial pressure  $P_i$  in the gas phase. Therefore, reaction rate  $r$  becomes:

$$r = k \theta_A \theta_B = \frac{k K_A K_B X_A X_B}{(1 + K_A X_A)(1 + K_B X_B)}$$

where  $k$  is the true rate constant. It has to be recalled that, besides the mass of catalyst, reaction rate constant  $k$ , in thermo-catalysis, exclusively depends on a single parameter: temperature!

$k = f(T)$  exclusively according to the Arrhenius' law:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \text{ with } E_a = \text{true activation energy.}$$

Similarly, adsorption constants  $K_i$  only vary with temperature  $T$  according to van t'Hoff's law

$$K_i = (K_i)_0 \exp\left(\frac{-\Delta H_i}{RT}\right)$$

where  $\Delta H_i$  is the enthalpy of adsorption of reactant  $i$ .

By contrast, the *true* rate constant in photocatalysis only depends on light intensity (or radiant flux). Indeed, the thermo-activation of the catalyst has been replaced by its photo-activation or, in other words, phonons have been replaced by photons. However, despite these essential assertions concerning thermo- and photocatalyses, it is not rare, alas, to find in the literature or in submitted articles that both  $k$  and  $K$  vary with concentration!

Generally, one of the two reactants (for instance B) is either in excess or maintained as constant. Therefore,  $\theta_B = 1$  or  $\theta_B = \text{constant}$ .  $\theta_B$  is equal to one for example in a pure reactant liquid phase;  $\theta_B$  is constant but  $<1$  for instance for oxygen in oxidation reactions either in ambient air ( $P_{O_2} \approx 1/5 \text{ atm}$ ) or in liquid phase through its dissolution via Henry's law. Therefore:

$$r = k \theta_B \theta_A = k' \theta_A = \frac{k' K_A C_A}{1 + K_A C_A}$$

with  $k' = k \theta_B$  = pseudo-true rate constant.

There are two limit cases:

- (i)  $C = C_{\max} \Rightarrow \theta_A = 1$  and thence  $r = k'$
- (ii)  $C \ll C_{\max} \Rightarrow \theta_A = (K_A C_A)/(1 + K_A C_A) \approx K_A C_A$  and thence  $r \approx k' K_A C_A = k_{\text{app}} C_A$  with  $k_{\text{app}}$  = apparent first order rate constant.

Activation energy can be deduced from the slope of the Arrhenius plot:

$$\frac{\partial \ln k_{\text{app}}}{\partial (1/T)} = -E_{\text{app}} R \Rightarrow E_{\text{app}} = E_a + \Delta H_A$$

Therefore, although the *true* rate constant in photocatalysis is independent of temperature but only depends on light intensity (or radiant flux), by contrast, the apparent 1st order rate constant depends on temperature because it includes an adsorption constant  $K$ , which is temperature dependent. This is why temperature has a small but real influence on photo-activity with generally an apparent activation energy of ca. 5 kcal/mol (20 kJ/mol). Again, it is not rare, alas, to read in the literature or in submitted articles that both  $k$  and  $K$  vary with concentration!

## HETEROGENEOUS PHOTO CATALYSIS

- 1) Transfer of the reactants in the fluid phase
- 2) Adsorption of the reactants at the surface of the catalyst
- 3) Reaction in the adsorbed phase
  - 3.1 Absorption of photons by the solid (no photochemistry)
  - 3.2 Creation of photo-induced electrons and holes
  - 3.3 Electron Transfer Reactions (Ionosorption, charge neutralization, radical formation, surface reactions...)
- 4) Desorption of the final products
- 5) Removal of the final products in the fluid phase

Fig. 2. The basic 5-step process common to heterogeneous catalysis and to heterogeneous photocatalysis.

### 3. Respect of the fundamentals of heterogeneous photocatalysis

#### 3.1. The five physical parameters governing photo-activity

The influence of the five physical parameters with govern the photocatalytic activity represented by the temporal reaction rate  $r$  is illustrated by Fig. 3.

In Fig. 3A, one can observe that the reaction rate  $r$  is proportional to the mass  $m$  of catalyst before reaching a plateau due to the full absorption of photons by the photocatalytic bed.

The initial proportionality between  $r$  and  $m$  is the same as that for conventional thermo-catalysis. This means that the activity or reaction rate is proportional to the total number of active sites  $n_t$  at the surface of the catalyst

$$n_t = m \times S_{\text{BET}} \times d_s$$

where  $S_{\text{BET}}$  is the specific area and  $d_s$  the areal density of sites whose maximum is estimated to be  $\leq 5 \times 10^{18}/\text{m}^2$  [11]. It has to be noted that the curve of Fig. 3A is quite general. Whatever the design of the photoreactor or the regime chosen (static or dynamic, slurry or fixed bed, solar or artificial light irradiation), the curve  $r=f(m)$  will always exhibit a linear variation followed by a plateau.

Such a curve should be determined in any study, in particular to determine the mass  $m_{\text{opt}}$  corresponding to the maximum absorption of photons reaching the catalytic bed.

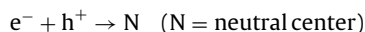
Fig. 3B represents  $r=f(\lambda)$ . Such a curve has to be established with monochromatic light and requires a pretty rapid reaction to have an accurate measurement of  $r$ .

It can be observed that this curve parallels that of the light absorption by the solid and enables one to determine the energy band gap  $E_G$  by catalytic measurements. Such a curve has to be confronted with thermodynamics as seen further.

Fig. 3C illustrates the Langmuir–Hinshelwood mechanism described above, whereas the Arrhenius plot of Fig. 3D directly depends from Fig. 3C as demonstrated in [2,3]. The two extreme cases can be qualitatively accounted for as follows. Since adsorption is a spontaneous and exothermic phenomenon, low temperatures favor adsorption including that of the final products which become inhibitors. On the opposite, high temperatures are detrimental for the adsorption of the reactants and the reaction rate declines [2,3,12].

Eventually, Fig. 3E illustrated the relationship  $r=f(\Phi)$ ,  $\Phi$  being the radiant flux of the light source (in  $\text{W}/\text{m}^2$ ). At moderate radiant

fluxes,  $r$  is proportional to  $\Phi$  below a maximum value, indicated by a dashed line, above which the rate declines from proportionality to follow a square root variation as  $r \propto \Phi^{1/2}$ . Such a change has been independently demonstrated in both Refs. [3,13] and indicated that too high radiant fluxes greatly increase the identical concentrations in photo-electrons and holes, which parabolically increases the recombination rate  $r_R$



$$r_R = k_R [e^-] [h^+] = k_R [e^-]^2$$

There is a loss (or a waste) in noble UV-light energy and the system does not operate in optimum conditions. In addition, since electron-hole recombination is exothermic, such high radiant fluxes may risk to increase the temperature of the catalyst, thus entering in the left-hand side domain in Fig. 3D where increasing temperatures make the reaction rate decline.

For information, an intense solar UV-radiant flux at noon in June Plataforma Solar de Almeria ( $37^\circ$  latitude) is close  $38 \text{ W}/\text{m}^2$  [14]. Using a Philips HPK 125 UV-lamp (125 electrical Watts), the change in regime from  $r \propto \Phi$  to  $r \propto \Phi^{1/2}$  was obtained at  $\Phi = 250 \text{ W}/\text{m}^2$ .

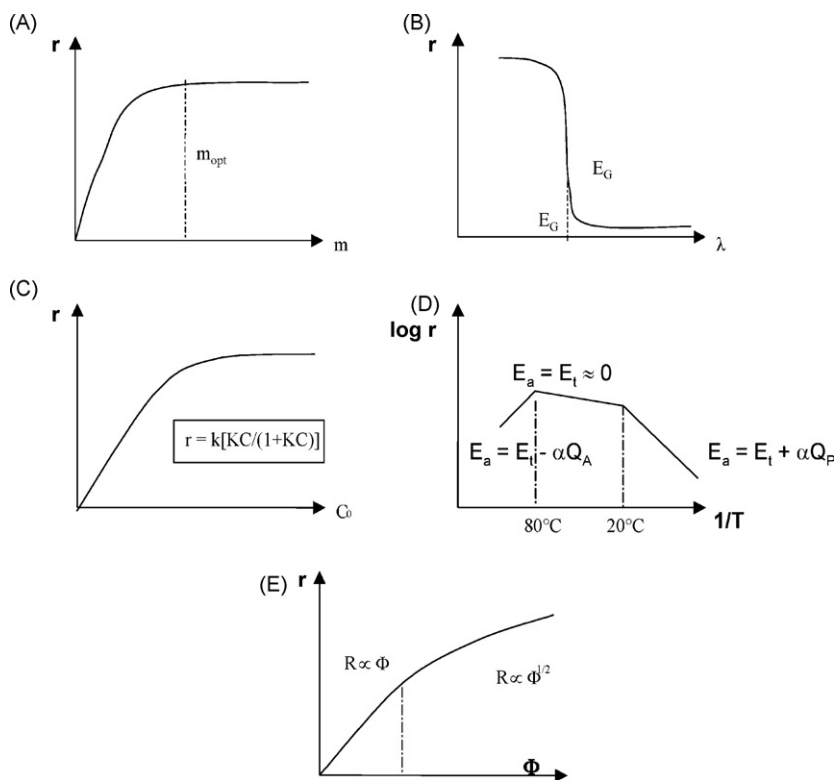
Therefore, it is counterproductive to use over-powered lamps especially with small photoreactors as often read in the literature.

#### 3.2. Quantum yield (QY) (or quantum efficiency)

Although it is dimensionless, (QY) is a “doubly kinetic” magnitude since it is defined as the ratio of two rates: the reaction rate  $r$  (in molecules converted/second) divided by the efficient photonic flux  $\varphi$  (in photons/second) absorbed by the solid

$$\langle \text{QY} \rangle = \frac{r}{\varphi}$$

This is an instantaneous magnitude directly linked to the parameters mentioned above, in particular to the concentration or partial pressure. The maximum value of (QY) will be obtained at maximum coverage of reactants (see plateau in Fig. 3C). The highest QY ever experimentally observed in our laboratory was ca. 0.40 (or 40%) in the case of methanol dehydrogenation in pure liquid phase, i.e. with  $C = 25 \text{ mol}/\text{L}$  [15]. On the contrary, for pollutant traces elimination, QY decreases mathematically to less than 1% ( $<0.01$ ), because of the Langmuir–Hinshelwood equation illustrated by Fig. 3C.



**Fig. 3.** Influence of the different physical parameters which govern the kinetics of photocatalysis: reaction rate,  $r$ ; (A) mass of catalyst  $m$ ; (B) wavelength  $\lambda$ ; (C) initial concentration  $c$  of reactant; (D) temperature  $T$ ; (E) radiant flux  $\Phi$ .

If the photonic flux  $\varphi$  (in efficient photons/second) is carefully determined from the radiant flux  $\Phi$ ,  $\langle QY \rangle$  is directly proportional to the slope of the first section of Fig. 3E.

As a concluding remark of this section, high  $\langle QY \rangle$  can only be obtained at full coverages in reactants. The high  $\langle QY \rangle$  values cited in the literature, that are obtained at very low pressures or concentrations, especially in diluted solutions or in trace elimination or with super-powerful UV-lamps, may appear as suspect.

### 3.3. Respect to kinetics: avoid confusion between reaction rate and conversion

In several articles, it is generally mentioned that the reaction rate  $r$  is (apparent) first order as expected from the initial part of Fig. 3C. Therefore, one should expect an increase in the rate  $r$  as concentration  $C$  increases. Very often in published or in submitted articles, a few lines further than the mention that “reaction rate  $r$  is of the first order”, it is written that the rate decreases when one increases the concentration. This surprising contradiction is due to the confusion between reaction rate  $r$  and conversion  $\tau$ !

Conversion  $\tau$  is defined as  $\tau = (C_0 - C)/C_0 = 1 - C/C_0$  and is generally expressed in %. It must be clearly understood that it is faster to eliminate say 50% of a solution of  $10^{-6}$  mol/L than 50% of a molar solution (1 mol/L) since a photocatalytic reaction is moderated by the photon fluxes delivered by the lamps.

Actually, in a true 1st order reaction, the integration of the reaction rate  $-dC/dt = kC$  gives  $C = C_0 \exp(-kt)$  or  $\ln(C/C_0) = -kt$ . Conversion  $\tau$  is independent of the initial concentration  $C_0$  but the rate and the number of converted molecules are indeed proportional to  $C_0$ .

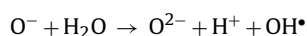
To illustrate this assertion, let us consider the effect of the initial concentration of *E. coli* on the photocatalytic disinfection efficiency of TiO<sub>2</sub> Degussa P-25 [16]. The bacterial survival of wild type *E.*

*coli* (*E. coli* 849), performed at different initial concentrations, is depicted in the semi-log plot of Fig. 4.

As expected, longer times are required for bacterial inactivation at higher bacteria concentrations. The semi-log<sub>10</sub> plot is necessary to present all the points for  $1 < C < 5 \times 10^7$  CFU/mL. It can be observed that, for the 3 lower curves, the initial slopes  $d \log C/dt$  for  $0 \leq t \leq 60$  min, are equal and correspond to  $-k/2.30$ ,  $k$  being the apparent 1st order reaction rate. By contrast, in the literature, similar curves have been briefly and crudely commented as: “the lower the concentration, the higher the reaction rate”! It has to be noted, that the upper straight line corresponds to a too high  $C_0$  ( $10^9$  CFU/mL) with a full coverage in *E. coli* and a consequent apparent zero order.

### 3.4. Respect to thermodynamics and to photonics

The energetics of photocatalysis is based on the energy  $E$  of the photons, i.e.  $E \geq 3.2$  eV. This energy represents 308 kJ/mol and/or 73.7 kcal/mol, i.e. a strong supply in energy. Consequently, it enables titania to produce very strong oxidizing agents, the photoholes  $h^+$ . This virtual positive charge is chemically supported by  $O^{2-}$  surface or bulk lattice anions of titania. This is the chemical oxidizing species, very strongly electrophilic. In particular, it is responsible for the generation, in presence of adsorbed water, of  $OH^\bullet$  radicals, the second best oxidizing agent after fluorine F



The temptation to decrease the photon energy towards the visible to “harvest the abundant visible energy spectrum of the sun” should take into account the necessity of passing over a minimum energy threshold since, otherwise, the activation would become thermodynamically detrimental for the generation of such highly cracking and degrading species that are  $OH^\bullet$  radicals



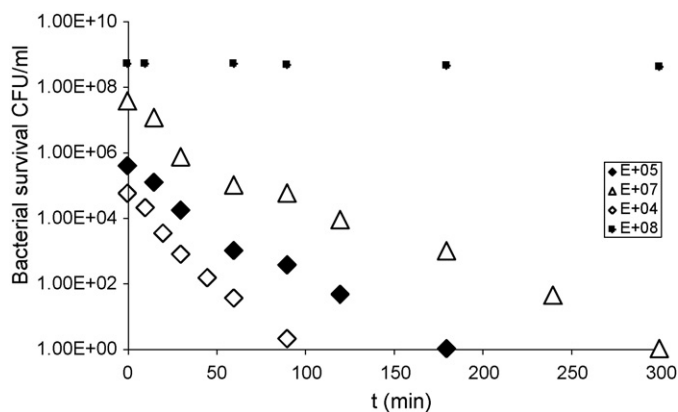


Fig. 4. Kinetics of the bacterial survival decrease of wild type *E. coli* in the presence of UV-irradiated TiO<sub>2</sub> Degussa P-25 at different initial concentrations.

### 3.5. True catalysis must exceed the “Stoichiometric Threshold”

For demonstrating the *true catalytic nature* of a photocatalytic reaction as suggested first by Pruden and Ollis [7], the conversion has to be carried out beyond a certain percentage corresponding to the catalytic threshold [12]. It is defined as the minimum number of molecules that have to be converted to be greater than the maximum number of potential active sites initially present at the surface of a mass  $m$  of titania photocatalyst used in the reaction. If we admit for titania that the maximum surface site density is equal to  $5 \times 10^{18}$  sites/m<sup>2</sup> according to Boehm [11], therefore one should obtain a minimum number  $n_{\min}$  of molecules converted equal to:  $n_{\min} = (5 \times 10^{18}) \times m \times S_{\text{(BET)}}$ . For example, if a photoreactor contains 1 g of titania Degussa P-25 (with  $S_{\text{(BET)}} = 50 \text{ m}^2/\text{g}$ ), which is fully illuminated and respects the laws mentioned above, a given photocatalytic reaction could be declared “truly catalytic” only if the number of converted molecules is higher than  $n_{\min} = (5 \times 10^{18}) \times m \times S_{\text{(BET)}} = 2.5 \times 10^{20}$  molecules, i.e.  $4.2 \times 10^{-4}$  mol. The conversion  $\tau$ , equal to  $\tau = (C_0 - C)/C_0 = (1 - C/C_0)$ , which depends on initial conditions of concentrations and pressures, must be higher than the value calculated from  $n_{\min} = 2.5 \times 10^{20}$  molecules, i.e.  $4.2 \times 10^{-4}$  mol. Actually, a true catalytic system should work with ratios  $n/n_{\min}$  of many orders of magnitude. In Ref. [15], ratios  $n/n_{\min}$  much higher than  $10^3$  could be obtained in alcohol dehydrogenation.

The test for the respect of the stoichiometric threshold is particularly important for dealing with a true catalytic process. In the problem of air and/or water purification, one is faced with traces elimination. The disappearance of such traces can be easily measured and quantified but disappearance does not mean degradation. It can also result from non-catalytic artifacts (adsorption, electron transfer, etc.) as evidenced in indigo carmine decoloration in the visible [17].

### 3.6. Mass balance determination

Since Lavoisier, it is known that “rien ne se crée, rien ne se perd, tout se transforme”, i.e. “nothing is created, nothing is lost, everything is transformed”. All the studies in photocatalysis, should include an exhaustive overall mass balance analysis. Two examples can explain this necessity. First, in the photocatalytic degradation of azo-dyes, the nitrogen mass balance, established on the final contents in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  could only exceed a few tens of percent [18–20]. A thorough complete analysis indicated an unsuspected evolution of gaseous nitrogen in the air. Actually, this amount of  $\text{N}_2(\text{g})$  corresponded to 100% of the  $-\text{N}=\text{N}-$  azo-groups in the molecule. Such a result underlines the environmentally friendly char-

acter of the degradation of azo-dyes, which represents 45% of the global industrial dye production.

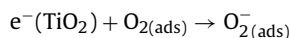
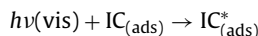
A second example concerns the degradation of pesticides and of dyes containing a strongly aromatic triazinic ring. Although the HPLC analyses indicated the formation of cyanuric acid  $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$  as the unique final product, the Total Organic Carbon (TOC) analyzer indicated a total conversion of the organic matter. The truth was that HPLC analyses were correct and that the TOC-analyzer was unable to destroy  $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$  into three  $\text{CO}_2$  molecules for their IR detection because of the too high stability of cyanuric acid. The consequence was that the assertion by Pelizzetti et al. according to which cyanuric acid could not be destroyed by photocatalysis, was still true [21].

Actually, the problem of TOC analyses with atrazine could be true 10 years ago but modern TOC-meters, based on catalytic combustion at high temperature ( $>700^\circ\text{C}$ ) are able to destroy triazinic ring. Therefore, this error must not happen today, because of the importance of using “high temperature-catalytic-combustion”-TOC analyzers when evaluating photocatalytic treatments. Not so consistent techniques such as low temperature-TOC analyzers, and COD should be given up.

### 3.7. True photocatalytic normalized tests

In line with the applications and commercialization of photocatalytic devices (air purifiers, domestic refrigerators, self-cleaning materials, etc.), photocatalytic normalized tests have to be clearly defined and disseminated. In addition to the above recommendations, a real photocatalytic activity test can be erroneously claimed if a non-catalytic side-reaction or an artifact does occur. Many tests are based on dyes decolorization, which is easy to perform with a UV-vis spectrophotometer. However, these tests can represent the most “subtle pseudo-photocatalytic” systems, hiding the actual non-catalytic nature of the reaction involved. This was quantitatively demonstrated with the apparent photocatalytic “disappearance” of indigo carmine dye [17]. Whereas indigo carmine IC was totally destroyed by UV-irradiated titania, its color also disappeared when using visible light. Actually, it was decolorized but its corresponding total organic carbon (TOC) remained intact. The loss of color actually corresponded to a limited stoichiometric transfer to titania of electrons originating from indigo molecules, photo-excited in the visible as  $\text{IC}^*$ . This is quite possible since the electronic energy level of  $\text{IC}^*$  is higher than that of the conduction band of titania.

This electron transfer destroys the regular distribution of conjugated bonds within the dye molecule and causes its decolorization. Once transferred to titania, the electron will participate to an additional iono-sorption of molecular oxygen as  $\text{O}_2^-$ . This is described by the following equations and illustrated by Fig. 5



When the same reaction was performed with a higher concentration of IC providing an initial number of molecules higher than the stoichiometric threshold described above, the solution remained totally colored with indeed the same constant initial TOC value.

As a consequence, all standardization test, exclusively based on dye decolorization, should be banished and it is recommended to test photocatalysts using different molecules such as isopropanol, phenols, aliphatics, N-containing compounds, etc. and not only measuring parent compounds disappearance but also their

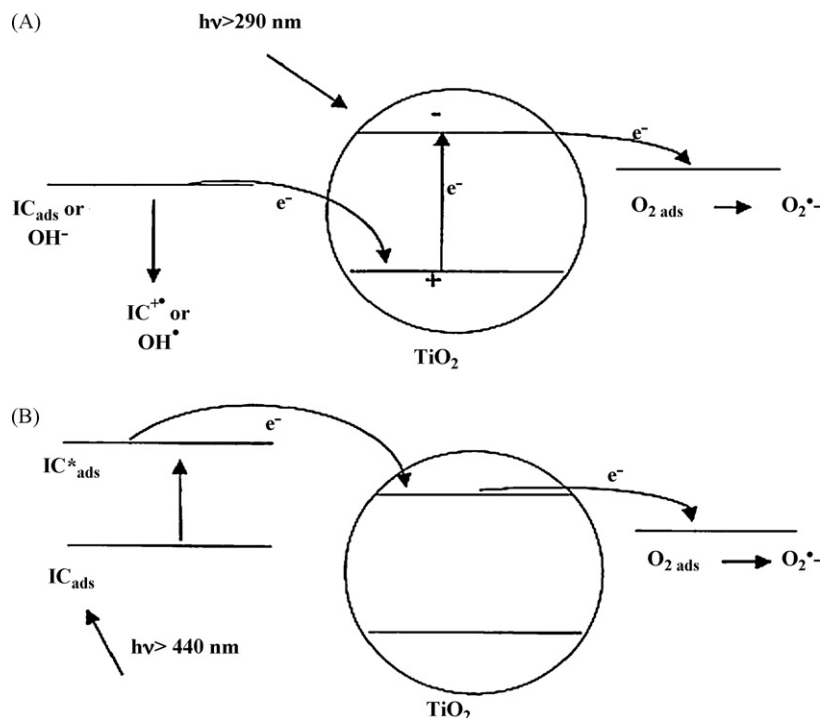


Fig. 5. Degradation of Indigo Carmine dye under UV-irradiation (A) and electron transfer from excited IC\* molecules without hole formation under visible light (B).

mineralization by TOC determination, before stating the real photocatalytic activity of a solid.

### 3.8. Respect to solid state chemistry

Photocatalytic studies on doping have been numerous, even too numerous. It has to be reminded that doping consists in dissolving controlled and moderate quantities of heterovalent cations in lattice sites of Ti<sup>4+</sup> host cations to apply the “induction valence law” defined in electronics [22]. It is now generally and finally admitted that cationic doping is detrimental for photocatalysis. Chromium doping was catastrophic [23]. This was clearly and quantitatively explained by the fact that doping cations act as recombination centers [3b].

Anionic doping has been a new innovative concept with the narrowing of the band gap energy [24,25]. For nitrogen doping (N-doping  $\neq$  n-type doping), it must be proved (i) that nitrogen should be present in a nitride state N<sup>3-</sup>, (ii) that N<sup>3-</sup> anions are in O<sup>2-</sup> lattice bulk positions and (iii) that, in oxidizing working conditions,

titania has no tendency to self-clean by reoxidizing and expelling N<sup>3-</sup> anions with a favorable decrease of the ionic radius of element N from 1.71 Å to 0.55, 0.25, 0.16 and 0.13 Å for −3, 0, +1, +3 and +5 oxidation number of N, respectively.

### 3.9. Erroneous schematic diagram

Several illustrations are erroneous or misleading. Two examples are given.

#### 3.9.1. Energy band diagram

In almost all reviews or introductions on photocatalysis, including my previous own ones [3a], the energy band diagram is generally presented in the shape of Fig. 6. I realized that it was not logical nor homogeneously presented, when once I was asked by a colleague to explain it.

This representation is wrong since it mixes an allegoric catalyst particle geometry with and into an energy band diagram of titania with the electron energy plotted upwards. Such a representation

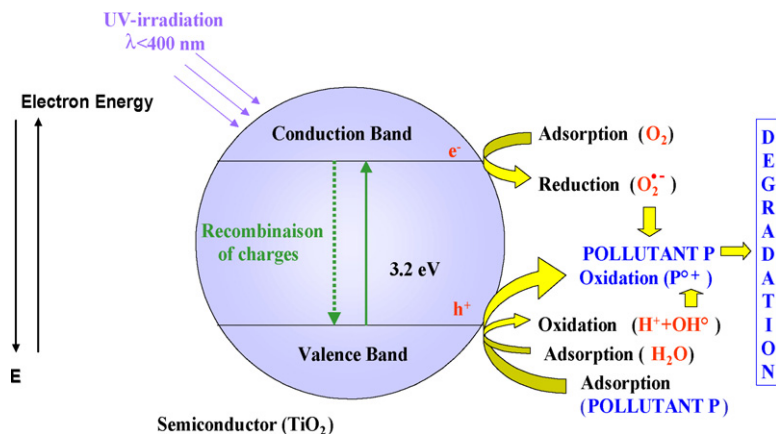


Fig. 6. Misleading titania's energy band diagram, commonly and generally adopted.

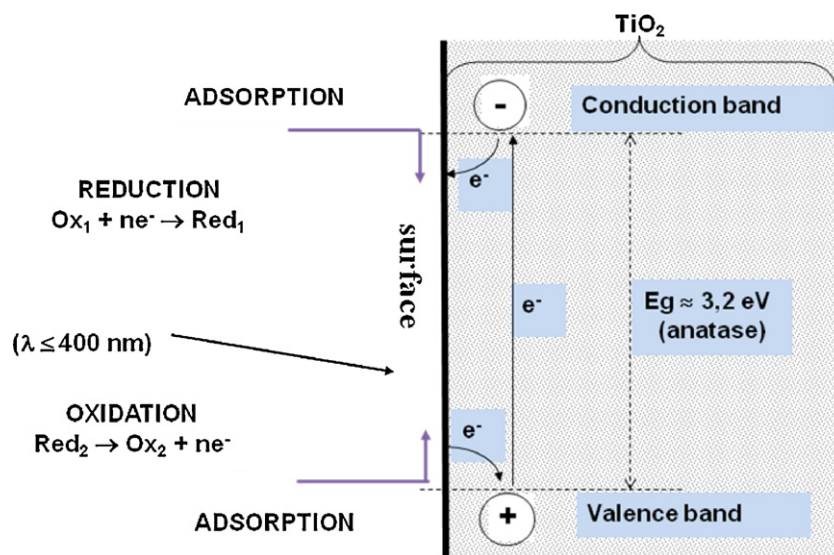


Fig. 7. Electron energy plotted upwards as a function of the distance from the surface to the bulk of the solid.

cannot be understood by a non-initiated reader, as I experimentally checked several times. In addition, it is wrong since the round arrows seem to indicate that the photoexcited species formed at the surface escape from this surface to react in the ambient (gas or liquid) fluid phase, which is contrary to a true heterogeneous catalytic process.

A less aesthetic but more realistic model is given in Fig. 7 with a diagram of the electron energy as a function of the distance from the surface to the bulk of titania.

As a consequence, photocatalysis mechanism must not be illustrated any more by Fig. 6, which looks pretty well presented but misleading since it is more in line with molecular and homogeneous catalyses.

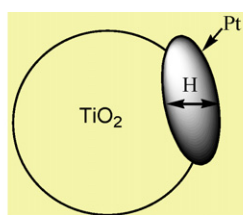
### 3.9.2. Description of bifunctional Pt/TiO<sub>2</sub> photocatalysts for hydrogen-involving reactions

Many articles mention the addition of a noble metal, mainly Pt, to hypothetically improve the photocatalytic activity of titania. Actually, the addition of Pt is only working with bifunctional Pt/TiO<sub>2</sub>

photocatalysts for hydrogen-involving reactions [15,26]. Moreover, it has been semi quantitatively shown that Pt is indispensable for hydrogen production in reducing conditions, was oppositely detrimental for oxidation reactions [27].

Very often the preparation of Pt/TiO<sub>2</sub> photocatalysts is not accurate enough and it is not sure whether the final Pt/TiO<sub>2</sub> photocatalysts, especially those obtained by photodeposition, are irreversibly stable, as those obtained in conventional catalysis with reduction by hydrogen [15]. One has to be sure if there remain some cations such as Pt<sup>IV</sup> or Pt<sup>2+</sup> on titania, which could later play the role of hidden oxidants when reducing to Pt<sup>0</sup>, thus conferring to this catalysts undue activity. Generally, they are poorly characterized by contrast with conventional heterogeneous catalysis for hydrocarbons and hydrogen.

Many references illustrate their Pt/TiO<sub>2</sub> catalysts as in Fig. 8. Such a representation is totally erroneous as evidenced by TEM electron microscopy. Platinum deposited on titania via the recipes of conventional and industrial catalysis is generally present as small particles of 1–2 nm. It is characterized by its dispersion D, corre-



H	Pt wt %
R/2	140
R/3	93
R/4	70
R/10	28

$$\text{Volume of Pt : } V_{\text{Pt}} = \frac{2}{3} \pi R^2 H$$

$$\text{if } H = R/2 \Rightarrow V_{\text{Pt}} : \pi R^3/3$$

$$\frac{V_{\text{Pt}}}{V_{\text{TiO}_2}} = 1/4$$

$$\frac{m_{\text{Pt}}}{m_{\text{TiO}_2}} = \frac{\rho_{\text{Pt}}}{\rho_{\text{TiO}_2}} \times \frac{V_{\text{Pt}}}{V_{\text{TiO}_2}} = 1.40$$

Pt wt% = 140%

Best Pt/TiO<sub>2</sub> = 0.5 wt%

1 particle of Pt (1.2 nm) / particle TiO<sub>2</sub> (Degussa)

⇒ Error factor : 280 !

Fig. 8. Erroneous schematic representation of Pt/TiO<sub>2</sub> (for explanations, see text).

sponding to the ratio of the number of surface metal atoms  $n_s$  to the total number  $n_T$  of metal atoms present

$$D = \frac{n_s}{n_T}$$

$D$  can be easily measured with simple reactions such as hydrogen chemisorption, oxygen chemisorption or  $H_2$ – $O_2$  titrations [28]. Assuming a population of homodispersed (i.e. with the same size) metal particles, the mean particle size  $d$  expressed in nanometer could be easily related to dispersion  $D$  by the simple equation:

$$d(\text{nm}) \approx \frac{1}{D}$$

Actually, unity in the numerator is not fortuitous but results from the mean surface density of metal atoms, which is almost constant for transition metals [28,29]. For example, a metal with a dispersion of 0.8 (or 80%) is present under the shape of particles having a mean diameter of 1.2 nm. All these results were confirmed by transmission electron microscopy (TEM) [26].

If one considers the purely speculative scheme in Fig. 8, one can calculate the corresponding metal loading. According to the shape given to Pt deposit, it can be assimilated to a spherical calotte, whose volume is equal to  $2/3\pi R^2 H$ . In Fig. 8, a table gives the calculated Pt loadings as a function of the thickness  $H$ , expressed in radius fractions. This clearly demonstrates that the model in Fig. 8 is quite unrealistic. In particular, if one considers that the optimum Pt/TiO<sub>2</sub> be functional photocatalysts contains 0.5 wt% Pt [26], the calculation gives an error factor equal to 280 if thickness  $H$  is chosen equal to  $H = R/2$ .

All these results confirm that transmission electron microscopy (TEM) examinations with many electronic micrographs are a pre-requisite to invoke platinum (or noble metals) in Pt/TiO<sub>2</sub> photocatalysts!

#### 4. Conclusions

This article was aimed at underlining some misconceptions in studies on photocatalysis originating from scientists whose main field is not heterogeneous catalysis. The following protocol can be proposed to make a check up before initiating an experimental work and/or its interpretation.

- (1) Check that the photoreactor is operating with a mass of catalyst close to  $m_{\text{opt}}$ , the optimum mass shown in Fig. 3A, which directly depends of the photoreactor design.
- (2) Avoid to use over-powered lamps, especially with small photoreactors, since (i) the photocatalytic regime is less efficient as seen in Fig. 3E and (ii) side-effects can occur, principally thermal ones as illustrated in Fig. 3D.
- (3) Consider that maximum quantum yields  $\langle QY \rangle$  can only be obtained at full surface coverages in reactants.  $\langle QY \rangle$  values, obtained at very low pressures or concentrations, especially in diluted solutions or in trace elimination, must be mathematically very low, according to  $\langle QY \rangle$  definition.
- (4) Avoid confusion between reaction rate  $r = -dC/dt$  and conversion  $\tau = (C_0 - C)/C_0$ .
- (5) Demonstrate the true catalytic nature of a photocatalytic reaction by reaching a high enough conversion to convert a number of molecules higher than the initial number of adsorptive or active sites. The latter number is defined as the “catalytic threshold”.
- (6) Do not use dubious standardization tests based on non-truly photocatalytic systems such as dye decolorization, despite their facile use.
- (7) Avoid too simple analytical techniques when evaluating a complex process as photocatalytic degradation of pollutants, claiming that it is an environmental friendly process. Nowadays, these processes must be evaluated using consistent analytical tools.
- (8) Avoid well presented but misleading illustrations for photocatalytic mechanisms, which are not correct with respect to thermodynamics and heterogeneous catalysis.
- (9) The use of transmission electron microscopy (TEM) is a pre-requisite to characterize platinum Pt/TiO<sub>2</sub> (or noble metals) bifunctional photocatalysts.
- (10) Cationic doping of titania is rather detrimental for catalysis and should avoided.

In conclusion, all these recommendations have to be addressed before claiming that one deals with a true photocatalytic reaction, operated in suitable conditions.

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